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VERIFICATION

I, Kazuo Asahi, of Asahi & Masuda of Nishi-Shinbashi Noa Building 4F & 5F of 18-9, Nishi-Shinbashi 1-chome, Minato-ku, Tokyo 105-0003 Japan do solemnly and sincerely verify that I understand well both Japanese and English languages and that the attached document in English language is full and faithful translation of the copy of Japanese Patent Application No. 9-191681 filed on July 16, 1997.



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COMPOSITION FOR AN ORGANIC EL ELEMENT AND METHOD OF
MANUFACTURING THE ORGANIC EL ELEMENT

[CLAIMS]

[Claim 1] A composition for an organic EL element formed into a pattern by an ink-jet method, wherein the composition for an organic EL element is characterized by including as its main component a precursor of a conjugated organic polymer compound for forming a luminescent layer and at least one kind of fluorescent dye for changing the luminescence characteristic of said luminescent layer.

[Claim 2] The composition for an organic EL element as set forth in claim 1, wherein said luminescence characteristic is a maximum wavelength of light absorption.

[Claim 3] The composition for an organic EL element as set forth in claim 1 or claim 2, wherein said precursor of the conjugated organic polymer compound includes a polyarylene vinylene precursor.

[Claim 4] The composition for an organic EL element as set forth in claim 3, wherein said polyarylene vinylene precursor includes a precursor of a polyparaphenylene vinylene or its derivative.

[Claim 5] The composition for an organic EL element as set forth in any one of Claims 1-4, wherein said fluorescent dye includes rhodamine or rhodamine derivative.

[Claim 6] The composition for an organic EL element as set forth in any one of Claims 1-4, wherein said fluorescent dye includes distyrylbiphenyl and its derivative.

[Claim 7] The composition for an organic EL element as set forth in any one of Claims 1-4, wherein said fluorescent dye includes coumarin or coumarin derivative.

[Claim 8] The composition for an organic EL element as set forth in any one of Claims 1-4, wherein said fluorescent dye includes tetraphenylbutadiene (TPB) or tetraphenylbutadiene derivative.

[Claim 9] The composition for an organic EL element as set forth in any one of Claims 1-4, wherein said fluorescent dye includes quinacridone or quinacridone derivative.

[Claim 10] The composition for an organic EL element as set forth in any one of Claims 1-4, wherein said precursor and said fluorescent dye exist in the state of being dissolved or dispersed into a polar solvent.

[Claim 11] The composition for an organic EL element as set forth in any one of Claims 1-8, wherein the amount of said fluorescent dye to be added is 0.5 to 10wt% with respect to a solid component of the precursor of the conjugated organic polymer compound.

[Claim 12] The composition for an organic EL element as set forth in any one of Claims 1-11, wherein said composition includes a lubricant.

[Claim 13] A method of manufacturing an organic EL element by using the composition for an organic EL element in any one of claims 1-12, which is characterized by including the steps of forming a pattern by jetting said composition from a head by an ink-jet method; and forming a luminescent layer by polymerizing said precursor in said composition by heat treatment.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a composition for an electroluminescent (EL) element, and more particularly to a composition for an organic EL element.

[0002]

[Prior Art]

An organic EL element has a constitution in which a cathode and an anode are connected to the opposite sides of a solid thin film containing a fluorescent organic compound. When a voltage is applied across the electrodes, electrons and holes are injected into the thin film, and they migrate according to the generated electric field and recombine with each other. At the time, excitons are produced by the energy liberated upon the recombination, and energy (in the form of fluorescence or phosphorescence) is emitted when the excitons are returned to the ground state thereof. This phenomenon is called electroluminescence.

[0003]

The characteristic of an organic EL element resides in the point that a high luminance surface emission of 100 to 100,000cd/m² is possible at a low voltage of not more than about 10V. Further, the use of organic compounds affords the excellent advantage of an unlimited possibility as to the selection of raw materials, which cannot be found in other material systems. In other words, by appropriate selection of the kinds of the fluorescent materials, it is possible to realize emission of any visible rays ranging from blue color to red color.

[0004]

Here, a luminescent layer bears an important part for the

luminescence efficiency and the stability of the element. In the past, doping of high efficiency fluorescent dyes into the luminescent layer has been carried out in order to improve the luminescence efficiency and change the emission wavelength.

[0005]

The conventional organic EL element mainly uses a low molecular dye (host material), and it is formed into a thin film to form a laminated type organic thin film EL element. Such an organic thin film EL material is formed by adding a fluorescent dye to a low molecular weight host material, for example, an element obtained by adding a fluorescent dye such as perylene or distyrylbiphenyl or the like to a host material such as aluminum quinolynol complex (Alq₃) or distyrylbiphenyl or the like is mentioned.

[0006]

In order to form such a low molecular dye into a thin film, a vapor deposition method has been so far employed. However, it is difficult to obtain a homogeneous defect-free thin film by the vapor deposition method, and the formed thin film has a problem in its stability and strength. Specifically, there is a problem in that when increasing the temperature of the element, crystallization and cohesion of organic molecules occur and the crystallized spot can not make contact with the electrode, causing a nonluminous spot (so-called dark spot). Further, it can not be said that the vapor deposition method is an effective method for manufacturing an element, because it takes long time to form several organic layers using the vapor deposition method.

[0007]

[Problem to be Solved by the Invention]

It is an object of the present invention to provide a

composition for an organic EL element and a method of manufacturing such an organic EL element which can perform a high precision patterning in a simple manner and in a short time, achieve an optimization of a film design and a luminescence characteristic easily, and facilitate an adjustment of a luminescence efficiency, as well as form a thin film having excellent durability.

[0008]

[Means for Solving the problem]

Such an object is achieved by the present invention as follows from (1) to (13).

[0009]

(1) A composition for an organic EL element formed into a pattern by an ink-jet method, wherein the composition for an organic EL element is characterized by including as its main component a precursor of a conjugated organic polymer compound for forming a luminescent layer and at least one kind of fluorescent dye for changing the luminescence characteristic of the luminescent layer.

[0010]

(2) The composition for an organic EL element as set forth in (1) in the above, wherein the luminescence characteristic is a maximum wavelength of light absorption.

[0011]

(3) The composition for an organic EL element as set forth in (1) or (2) in the above, wherein the precursor of the conjugated organic polymer compound includes a polyarylene vinylene precursor.

[0012]

(4) The composition for an organic EL element as set forth in (3) in the above, wherein the polyarylene vinylene precursor includes a precursor of a polyparaphenylene vinylene or its derivative.

[0013]

(5) The composition for an organic EL element as set forth in any one of (1)-(4) in the above, wherein the fluorescent dye includes rhodamine or rhodamine derivative.

[0014]

(6) The composition for an organic EL element as set forth in any one of (1)-(4) in the above, wherein the fluorescent dye includes distyrylbiphenyl and its derivative.

[0015]

(7) The composition for an organic EL element as set forth in any one of (1)-(4) in the above, wherein the fluorescent dye includes coumarin or coumarin derivative.

[0016]

(8) The composition for an organic EL element as set forth in any one of (1)-(4) in the above, wherein the fluorescent dye includes tetraphenylbutadiene (TPB) or tetraphenylbutadiene derivative.

[0017]

(9) The composition for an organic EL element as set forth in any one of (1)-(4) in the above, wherein the fluorescent dye includes quinacridone or quinacridone derivative.

[0018]

(10) The composition for an organic EL element as set forth in any one of (1)-(4) in the above, wherein the precursor and the fluorescent dye exist in the state of being dissolved or dispersed into a polar solvent.

[0019]

(11) The composition for an organic EL element as set forth in any one of (1)-(8) in the above, wherein the amount of the fluorescent dye to be added is 0.5 to 10wt% with respect to a solid component of the precursor of the conjugated organic polymer compound.

[0020]

(12) The composition for an organic EL element as set forth in any one of (1)-(11) in the above, wherein the composition includes a lubricant.

[0021]

(13) A method of manufacturing an organic EL element by using the composition for an organic EL element in any one of (1)-(12) in the above, which is characterized by including the steps of forming a pattern by jetting the composition from a head by an ink-jet method; and forming a luminescent layer by polymerizing the precursor in the composition by heat treatment.

[0022]

[Embodiments of the invention]

Hereinbelow, a composition for an organic EL element according to the present invention will be described in detail.

[0023]

The composition for an organic EL element of the present invention is a composition for an organic EL element which is formed into a pattern by an ink-jet method, which includes a precursor of a conjugated organic polymer compound (hereinafter, referred to as "precursor") for mainly forming a luminescent layer and at least one kind of fluorescent dye for changing the emission characteristic of the luminescent layer.

[0024]

The precursor means a material which can be formed into a thin film as a composition for the organic EL element together with a fluorescent dye and the like and then produced a conjugated organic polymer EL layer by heating and hardening as shown, for example, by the following chemical formula (I). For example, when the precursor is a sulfonium salt, an elimination of the sulfonium group is caused by a heat treatment, thereby being turned into the conjugated organic polymer compound.

[0025]

[Chemical Formula (I)]

[0026]

Such a conjugated organic polymer compound exhibits a strong fluorescence in the solid state, and is capable of forming a homogeneous solid super thin film. Further, the conjugated organic polymer compound has an excellent formability, and has a high adhesion to an ITO electrode. In addition, such a precursor of the compound can form a sturdy conjugated polymer film after hardening, so, since a precursor solution (emulsion) can be adjusted to a desired viscosity suitable for ink-jet pattern formation as described later before heating and hardening, it is possible to form the thin film based on the optimum conditions easily in a short time.

[0027]

As for example of such a precursor, a polyarylene vinylene precursor is preferable. Since the polyarylene vinylene precursor is soluble in water or an organic solvent and such a precursor can be polymerized, it is possible to obtain a thin film having high optical quality.

[0028]

Examples of such a polyarylene vinylene precursor include:

precursor of PPV derivative such as PPV (poly(para-phenylene vinylene)) precursor, MO-PPV (poly(2,5-dimethoxy-1,4-phenylene vinylene)) precursor, CN-PPV (poly(2,5-bis(hexyloxy)-1,4-phenylene-(1-cyanovinylene))) precursor, MEH-PPV (poly[2-methoxy-5-(2'-ethylhexyloxy)]-para-phenylene vinylene) precursor and the like; poly(alkylthiophene) precursor such as PTV (poly(2,5-thienylene vinylene)) precursor and the like; PFV (poly(2,5-furylene vinylene)) precursor; poly(paraphenylene) precursor; and polyalkylfluorene precursor, and the like. Among these precursors, the precursor of PPV or its derivatives such as shown in the following chemical formula (II) is especially preferable.

[0029]

[Chemical Formula (II)]

[0030]

The precursor of PPV or PPV derivative is soluble in water, and is polymerized by heating after formation of a film thereof to form a PPV layer. Further, since PPV possess a strong fluorescence and it is also a conductive polymer in which π -electron of double bond is delocalized on the polymer chain, it is possible to obtain an organic EL element having high performance.

[0031]

The content of the precursor represented by the PPV precursor is preferably 0.01 to 10.0wt%, and more preferably 0.1 to 5.0wt%, with respect to the total amount of the composition. If the amount of the precursor to be added is too small, it is insufficient for formation of the conjugated polymer film, and if the amount of the precursor to be added is too much, there is a case that the viscosity of the composition becomes high, and therefore it is not suitable for pattern formation with high

precision by the ink-jet method.

[0032]

Further, the composition for an organic EL element according to the present invention includes at least one kind of fluorescent dye. This makes it possible to change the luminous property of the luminescent layer and is also effective as a means, for example, for improving the luminous efficiency of the luminescent layer or for changing the maximum wavelength of light absorption (emitted color) of the luminescent layers.

[0033]

Namely, a fluorescent dye can be utilized not only as a material for the luminescent layers but also as a material for the coloring matter which exhibits the luminescence function by itself. This is because almost all of the energy of the excitons which are generated by the recombination of carriers on the molecules of a conjugated organic polymer compound can be transferred onto the molecules of the fluorescent dye. In this case, the current quantum efficiency of the EL element is also increased, because the luminescence arises only from the molecules of the fluorescent dye which have a high fluorescence quantum efficiency. Accordingly, by addition of a fluorescent dye into the composition for the organic EL element, the luminescence spectrum of the luminescent layer becomes the spectrum of the fluorescent dye, thereby enabling to be effective as a means for changing the emitted color.

[0034]

Now, what is meant here by the current quantum efficiency is a scale for considering the luminescence performance according to the luminescence function, and it is defined by the following expression.

[0035]

η_E = energy of emitted photon / inputted electrical energy

[0036]

In this way, by changing the maximum wavelength of light absorption by doping of fluorescent dye, it becomes possible, for example, to emit the three primary colors of red, green and blue, thereby enabling to obtain a full color display device.

[0037]

Further, the doping of the fluorescent dye also makes it possible to improve extremely the luminous efficiency of the EL element.

[0038]

As for a fluorescent dye, rhodamine or a rhodamine derivative for generating red emitted color is preferably used. These fluorescent dyes are soluble in aqueous solutions because they are low molecules, and have a high compatibility with PPV, so that a luminescent layer with a good uniformity and good stability can be formed easily.

[0039]

As for examples of such fluorescent dyes, rhodamine B, rhodamine B base, rhodamine 6G, and rhodamine 101 perchlorate and the like can be mentioned, and a mixture of two or more of them can be employed.

[0040]

Further, as for a fluorescent dye, quinacridone and its derivative for generating green emitted color are preferably used. Since these fluorescent dyes are low molecules likewise the red fluorescent dyes, they are soluble in aqueous solutions and have a high compatibility with PPV, so that the luminescent layer can be formed easily.

[0041]

Further, as for the fluorescent dye, distyrylbiphenyl and its derivative for generating blue emitted color are preferable. These fluorescent dyes are soluble in aqueous solutions likewise the red fluorescent dyes, and have high compatibility with PPV, so that the luminescent layer can be formed easily.

[0042]

Further, as for other fluorescent dyes for generating blue emitted color, coumarin and its derivative are preferable. These fluorescent dyes are soluble in aqueous solutions because they are low molecules likewise the red fluorescent dyes, and have high compatibility with PPV, so that the luminescent layer can be formed easily.

[0043]

As for examples of such fluorescent dyes, coumarin, coumarin-1, coumarin-6, coumarin-7, coumarin 120, coumarin 138, coumarin 152, coumarin 153, coumarin 311, coumarin 314, coumarin 334, coumarin 337, coumarin 343 and the like can be mentioned.

[0044]

Further, as for other fluorescent dyes for generating blue emitted color, tetraphenylbutadiene (TPB) or TPB derivative are preferable. These fluorescent dyes are soluble in aqueous solutions because they are low molecules likewise the red fluorescent dyes, and have high compatibility with PPV, so that the luminescent layer can be formed easily. These fluorescent dyes as described above can be selectively used alone or in the form of a mixture of two or more of them.

[0045]

The amount of these fluorescent dyes to be added to the solid component of the precursor of the conjugated organic

polymer compound are preferably 0.5 to 10w%, and more preferably 1.0 to 5.0wt%. If the amount of the florescent dye to be added is too much, it becomes difficult to maintain the weather resistance and the durability of the luminescent layer. On the other hand, the amount of the florescent dye to be added is too little, it is impossible to obtain sufficiently the effect obtained by adding the florescent dye as described above.

[0046]

Moreover, it is preferable that the precursor and the fluorescent dye are dissolved or dispersed into a polar solvent. The polar solvent is capable of readily dissolving or homogeneously dispersing the precursor and the fluorescent dye or the like, and this makes it possible to prevent the solid component in the organic EL composition from being stuck at the nozzle hole of an ink-jet device and to prevent the nozzle hole from being clogged with the solid component, and also contributes to maintain the high contact angle of the ink at the nozzle hole. In this way, so that it is possible to prevent the bend in the jetted direction of the ink.

[0047]

As for examples of the polar solvent, water; water compatible alcohol such as methanol, ethanol and the like; organic solvents such as N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP), dimethylimidazoline (DMI), dimethylsulfoxide (DMSO) and the like; and inorganic solvents can be mentioned, and a mixture of two or more of these solvents can be employed as required.

[0048]

In addition, it is preferred that a lubricant is added in the composition for the organic EL element. In this way, it is

possible to prevent effectively the composition from being dried and solidified at the ink-jet nozzle hole. As for examples of such a lubricant, polyhydric alcohols such as glycerin and diethylene glycol and the like can be mentioned, and it is possible to use a mixture of two or more of them. The amount of the lubricant to be added is preferably about 5 to 20wt% with respect to the total amount of the composition.

[0049]

Moreover, other additives and film stabilizing materials may also be added, and for example, stabilizer, anti-aging agent, pH adjusting agent, antiseptic agent, resin emulsion, leveling agent or the like may be added.

[0050]

The composition for an organic EL element including the above-mentioned precursor and fluorescent dye is formed into a pattern by an ink-jet method.

[0051]

Here, the manufacturing method of an EL element by the ink-jet printing means a method for forming pixels with at least one color selected from the three primary colors comprising red, green, and blue and their intermediate colors by discharging the aforementioned composition, which is dissolved or dispersed into a solvent, as a discharge liquid from the head.

[0052]

According to the ink-jet printing method, a fine pattern formation can be carried out simply in a short time. In addition, depending on the discharging amount, the adjustment of film thickness can be done easily, so that film properties, emission balance and luminance and the like can be controlled readily and arbitrarily.

[0053]

The method of manufacturing the organic EL element according to the present invention is characterized by including a step of forming a pattern by jetting out the above-mentioned composition from the head by the ink-jet method, and a step of forming a luminescent layer by polymerizing the above-mentioned precursor of the above-mentioned composition by a heat treatment. According to this method, since the precursor of the conjugated organic polymer compound, which is prior to polymerizing, is used as a material, the degrees of freedom in the selection for viscosity of the composition material become large, so that it is possible to adopt the ink-jet method. Accordingly, since it is possible to jet an arbitrary amount of the composition solution to an arbitrary position, the emission characteristics and the film properties of the luminescent layer can be easily controlled.

[0054]

The structure of the head of the ink-jet device used in the manufacturing method of the organic EL element according to the present invention is shown in Fig. 2.

[0055]

The head 10 for the ink-jet device is provided with, for example, a stainless steel nozzle plate 11 and a vibration plate 13, and they are coupled via partitioning members (reservoir plates) 15.

[0056]

Between the nozzle plate 11 and the vibration plate 13, a plurality of spaces 19 and a liquid storage 21 are formed by means of the reservoir plates 15. The inside of the respective spaces 19 and the liquid storage 21 are filled with the composition according to the present invention, and the spaces 19

in communication with the liquid storage 21 through supply ports 23.

[0057]

Further, a nozzle hole 25 is provided in the nozzle plate 11 for discharging the composition in a jet-form from the spaces 19. On the other hand, a hole 27 is formed in the vibration plate 13 for supplying the composition to the liquid storage 21.

[0058]

Further, on a surface of the vibration plate 13 which is opposite to the surface that faces with the spaces 19, piezoelectric elements 29 are attached at positions corresponding to the positions of the respective spaces 19.

[0059]

When the piezoelectric element 29 is energized, the piezoelectric element 29 is bent to outside projectingly, and at the same time, the vibration plate 13 connected with the piezoelectric element 29 is bent to outside in a body with element 29. This increases the volume of the space 19. Therefore, the composition whose volume is equivalent to the increased volume in the space 19 is flowed in from the liquid storage 21 through supply the ports 23.

[0060]

Next, when the piezoelectric element 29 is stopped energizing, both the piezoelectric element 29 and the vibration plate 13 are brought back to the initial form. Consequently, since the volume of the space 19 is returned to the former volume, the pressure of the composition in the space 19 becomes high and the composition is jetted from the nozzle hole 25 toward the substrate.

[0061]

Now, it is preferable that a water repellent treatment such as Teflon coating treatment or the like are made at the inner wall portion of the nozzle hole 25 and its peripheral part in order to prevent the bend in the jetted direction of the composition and prevent clogging of the hole by the composition.

[0062]

Using the head described above, it is possible to form organic luminescent layers respectively by discharging the compositions corresponding to, for example, the three primary colors red, blue, and green according to predetermined patterns, thereby enabling to form the pixels.

[0063]

According to the ink-jet method as described above, the arbitrary amount of the composition, the number of times of the jet and the forms of patterns can be adjusted easily and handily, so that the luminescent characteristics and film thickness and the like of the luminescent layers can be controlled.

[0064]

Further, in the thin film formed in a manner described above, there is no problem such as the dark spot which appears in the vapor deposition method, so that it is possible to obtain an excellent EL element.

[0065]

[Embodiment]

In what follows, the present invention are described in details with reference to the actual examples.

[0066]

1. Manufacturing of Organic EL Element

(Example 1)

[0067]

Using the compositions for an organic EL element made from the compositions shown in Table 1 for respective colors, an organic EL element was manufactured by the method as shown in Fig. 1.

[0068]

[Table 1]

[0069]

As shown in Fig. 1, on the glass substrate 104, ITO transparent pixel electrodes 101, 102 and 103 were formed by means of photolithography so as to form respectively a pattern having a pitch of $100\mu\text{m}$ and a thickness of $0.1\mu\text{m}$. Then, a black resist polymer 105 which buries the spaces between the ITO transparent pixel electrodes and acts not only as a layer for cutting off the light but also as a wall for preventing ink drop are formed by photolithography. Each of the black resist was designed so as to have a width of $20\mu\text{m}$ and a thickness of $2.0\mu\text{m}$, respectively.

[0070]

Further, after the luminescent materials for the respective colors were coated to form patterns by jetting the compositions from the head 110 of an ink-jet printer device 109, they were undergone heat treatment under a nitrogen atmosphere at 150°C for 4 hours to polymerize the precursors in the compositions, thereby forming luminescent layers 106 (red), 107 (green) and 108 (blue) which emit red, green and blue respectively.

[0071]

Next, the vacuum deposition was carried out using the aluminum quinolynol complex to which no doping was carried out to form an electron transfer layer 111 having a thickness of $0.1\mu\text{m}$. This electron transfer layer 111 facilitates injection of the

electrons from the cathode, and contributes to the prevention of electrode quenching by keeping the luminescent portions away from the cathode to establish a better contact with the cathode.

[0072]

Finally, an Al - Li reflection electrode 112 having a thickness of $0.8 \mu\text{m}$ was formed as the counter electrode by the deposition method, thereby manufacturing the organic EL element.

[0073]

(Example 2)

An organic EL element was manufactured in the same way as in Example 1 except that quinacridone of 0.0075 wt% (ratio of the solid component of PPV precursor: 2%) was added into the green composition as a fluorescent dye.

[0074]

[Table 2]

[0075]

(Example 3)

An organic EL element was manufactured in the same way as in Example 1 except that rhodamine 101 was added into the red composition as a fluorescent dye.

[0076]

[Table 3]

[0077]

(Example 4)

An organic EL element was manufactured in the same way as in Example 1 except that coumarin 6 of 0.00375wt% and distyrylbiphenyl of 0.00375wt% (ratio of solid component of PPV precursor: 1wt%, respectively) were added into the blue composition as a fluorescent dye and that glycerin of 3wt% and diethylene glycol of 12wt% were used as a lubricant.

[0078]

[Table 4]

[0079]

(Example 5)

An organic EL element was manufactured in the same way as in Example 1 except that TPB (tetraphenylbutadiene) of 0.0075wt% (ratio of solid component of PPV precursor: 2wt%) was added into the blue luminescent layer composition as a fluorescent dye and quinacridone of 0.0075wt% (ratio of solid component of PPV precursor: 2wt%) was added into the green composition as a fluorescent dye, respectively, and that glycerin of 3wt% and diethylene glycol of 12wt% were used as a lubricant.

[0080]

[Table 5]

[0081]

(Example 6)

An organic EL element was manufactured in the same way as in Example 1 except that coumarin 138 was added into the blue composition as a fluorescent dye.

[0082]

[Table 6]

[0083]

(Example 7)

An organic EL element was manufactured in the same way as in Example 1 except that CN-PPV precursor which emits red color was added instead of PPV precursor without adding any red fluorescent dye and quinacridone of 0.0075wt% (ratio of solid component of PPV precursor: 2wt%) was added into the green composition as a fluorescent dye.

[0084]

[Table 7]

[0085]

(Comparative Example 1)

An omposition for an organic EL element formed of the composition shown in Table 8 were prepared, and then an organic EL element was manufactured by means of vacuum deposition method.

[0086]

[Table 8]

[0087]

(Comparative Example 2)

An composition for an organic EL element formed of the composition shown in Table 9 were prepared for respective colors, and then an organic EL element was manufactured in the same way as in Example 1.

[0088]

[Table 9]

[0089]

2. Evaluation of the Luminescence Characteristics and the Film Characteristics of the Luminescent Layers

The luminescence characteristics and the film characteristics of the respective luminescent layers of the organic EL elements which were manufactured according to Examples 1 to 7 and Comparative Examples 1 and 2 described above were evaluated according to the following methods.

[0090]

① Luminescence Starting Voltage

A prescribed voltage was applied to the element, and the applied voltage at which a luminance of 1 cd/m^2 is observed was defined as the luminescence starting voltage [Vth].

[0091]

② Luminescence Life

The initial luminance after a stabilization treatment has been carried out was set to 100%, and the changes in the luminance of the EL element were measured under the condition that the elements were kept in continuous luminescence by supplying a constant current of standard waveform, wherein the luminescence life is defined as the time until the luminance drops to 50% of the initial luminance. In this case, the drive conditions for this experiment were set at 40 °C for room temperature, 23% for humidity and 20 mA/cm² for current density.

[0092]

③ Luminance (Brightness)

The luminance was measured at which the current was set to 20 mA/cm².

[0093]

④ Wavelength at Maximum Absorption

The wavelength at maximum absorption for each luminescent layer was measured. Fig. 3 is a diagram which shows spectra at the luminescent layers of the organic EL element in Example 1.

[0094]

⑤ Stability in Film Formation

After heating the luminescent layer at 200 °C for 60 minutes, conditions for occurrence such as cracks and deformation and the like in the respective luminescent layers were observed by a microscope. The results of the evaluation are shown in Table 10 and Table 11.

[0095]

[Table 10]

[0096]

[Table 11]

[0097]

As indicated in Table 10 and Table 11, all of the luminescent layers in Examples 1 to 7 have excellent luminescence characteristics and excellent film characteristics. In contrast with these Examples, the stability in film formation of the luminescent layer in Comparative Example 1 was poor, and dark spots were observed therein. Further, for the luminescent layer in Comparative Example 2, the solvent of the composition, especially chloroform, eroded the parts constituting the head, and furthermore, since the composition tended to vapor due to the lower boiling point of chloroform so that a dry composition was adhered to cause the clogging of the nozzle, it was impossible to complete the formation of the pattern.

[0098]

In the above, the compositions for the organic EL element and the methods of manufacturing the organic EL elements have been described according to the respective embodiments illustrated. However, the present invention is not limited to these embodiments. Namely, it may further include a step of inserting arbitrary functional intermediate layers between the respective layers. Moreover, the fluorescent dye to be added for changing the luminescent characteristics is not limited to those of the embodiments as long as they can be dissolved and dispersed homogeneously into a polar solvent.

[0099]

[Effect of the Invention]

As described in the above, according to the compositions for an organic EL element of the present invention, a rational design of the organic EL element is possible through wide ranging selection of luminescent materials. Namely, by assorting a

conjugated organic polymer compound and a fluorescent dye, various kinds of light for display can be obtained, so that it is possible to realize a full color display. Accordingly, it is possible to develop designs for various organic EL elements with high luminance and long life.

[0100]

Further, since the precursor which is polymerized by heating and hardening is included as the luminescent layer material, conditions such as viscosity and the like can be freely set, and then the conditions suitable for a discharge liquid used for the ink-jet method can be easily adjusted.

[0101]

Further, according to the method of manufacturing the composition for organic EL element, conditions such as the film thickness, the number of dots and the like can be adjusted arbitrarily, so that the luminescence characteristics of the luminescent layers can be controlled easily. And, the size and the pattern of the luminescent element can also be set arbitrarily.

[Brief Description of the Drawings]

[Fig. 1]

This figure is a sectional view which shows steps performed in the method of manufacturing the organic EL element.

[Fig. 2]

This figure is a perspective view which shows an example of a configuration of a printer head of an ink-jet device which is used for manufacturing the organic EL element.

[Fig. 3]

This figure is a diagram which shows wavelength at

absorption of light in each of the luminescent layers of the organic EL element (Example 1) according to the present invention.

[Description of Symbols]

10	Head for the ink-jet device
11	Nozzle plate
13	Vibration plate
15	Reservoir plate
19	Space
21	Liquid storage
23	Supply port
25	Nozzle hole
27	Hole
29	Piezoelectric element
101	Transparent pixel electrode
102	Transparent pixel electrode
103	Transparent pixel electrode
104	Glass substrate
105	Polymer black resist
106	Organic luminescent layer (red)
107	Organic luminescent layer (green)
108	Organic luminescent layer (blue)
109	Ink-jet printer device
110	Head
111	Electron transfer layer
112	Counter electrode

[Document Name] Abstract

[Summary]

[Problem] Forming a high precision pattern is possible in a simple manner and in a short time, and the optimization of film design and luminescence characteristic can be easily performed, and then an adjustment of a luminescence efficiency can also be easily performed.

[Solving Means] A composition for an organic EL element formed into patterns by an ink-jet method which includes as its main component a precursor of a conjugated organic polymer compound for forming luminescent layers (106)-(108) and at least one kind of fluorescent dye for changing the luminescence characteristic of the luminescent layer. As for the precursor, for example, a precursor of polyphenylene vinylene or its derivative can be mentioned. As for the fluorescent dye, for example, rhodamine B, distyrylbiphenyl, coumarin, tetraphenylbutadiene, quinacridone, and their derivatives can be mentioned.

[Selected Drawings] Fig. 1

Table 1

(Example 1)

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
Composition	Amount of Content (wt%)		Composition	Amount of Content (wt%)		Composition	Amount of Content (wt%)	
	Precursor	PPV -precursor		Precursor	PPV -precursor		Precursor	PPV -precursor
Wetting Agent		glycerin	Wetting Agent		glycerin	Wetting Agent		glycerin
		diethylene -glycol			diethylene -glycol			diethylene -glycol
Polar Solvent		water	Polar Solvent		water	Polar Solvent		water
		methanol			methanol			methanol
		DMF			DMF			DMF
Fluorescent Dye		rhodamine B	Fluorescent Dye		distyryl -biphenyl	Fluorescent Dye		Without Fluorescent Dye
		(Ratio of Solid Portion of Precursor : 2 wt%)			(Ratio of Solid Portion of Precursor : 2 wt%)			—

Table 2

(Example 2)

Red Luminescent Layer		Blue Luminescent Layer		Green Luminescent Layer	
Composition	Amount of Content (wt%)	Composition	Amount of Content (wt%)	Composition	Amount of Content (wt%)
Precursor	0. 3 7 5	Precursor	0. 3 7 5	Precursor	0. 3 7 5
	ppv -precursor		ppv -precursor		ppv -precursor
Wetting Agent	5	Wetting Agent	5	Wetting Agent	5
	glycerin		glycerin		glycerin
	1 0		1 0		1 0
	diethylene -glycol		diethylene -glycol		diethylene -glycol
Polar Solvent	1. 2 3 1	Polar Solvent	1. 2 3 1	Polar Solvent	1. 2 3 1
	water		water		water
	methanol		methanol		methanol
	2 3. 3 9 4		2 3. 3 9 4		2 3. 3 9 4
	DMF		DMF		DMF
	6 0		6 0		6 0
Fluorescent Dye	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)
	rhodamine B		distyryl -biphenyl		quinacridone

Table 3

(Example 3)

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
Composition	Amount of Content (wt%)		Composition	Amount of Content (wt%)		Composition	Amount of Content (wt%)	
Precursor	ppv -precursor	0. 3 7 5	Precursor	ppv -precursor	0. 3 7 5	Precursor	ppv -precursor	0. 3 7 5
Wetting Agent	glycerin	5	Wetting Agent	glycerin	5	Wetting Agent	glycerin	5
	diethylene -glycol	1 0		diethylene -glycol	1 0		diethylene -glycol	1 0
Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1
	methanol	2 3. 3 9 4		methanol	2 3. 3 9 4		methanol	2 3. 3 9 4
	DMF	6 0		DMF	6 0		DMF	6 0
Fluorescent Dye	rhodamine 101	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	distyryl -biphenyl	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	Without Fluorescent Dye	—

Table 4

(Example 4)

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)
Precursor	PPV -precursor	0. 3 7 5	Precursor	PPV -precursor	0. 3 7 5	Precursor	PPV -precursor	0. 3 7 5
Wetting Agent	glycerin	3	Wetting Agent	glycerin	3	Wetting Agent	glycerin	3
	diethylene -glycol	1 2		diethylene -glycol	1 2		diethylene -glycol	1 2
Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1
	methanol	2 3. 3 9 4		methanol	2 3. 3 9 4		methanol	2 3. 3 9 4
	DMF	6 0		DMF	6 0		DMF	6 0
Fluorescent Dye	rhodamine B	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	coumarin 6	0. 0 0 3 7 5 (1 wt%)	Fluorescent Dye	Without Fluorescent Dye	—
				distyryl -biphenyl	0. 0 0 3 7 5 (1 wt%)			

Table 5

(Example 5)

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)
Precursor	PPV -precursor	0. 3 7 5	Precursor	PPV -precursor	0. 3 7 5	Precursor	PPV -precursor	0. 3 7 5
Wetting Agent	glycerin	3	Wetting Agent	glycerin	3	Wetting Agent	glycerin	3
	diethylene -glycol	1 2		diethylene -glycol	1 2		diethylene -glycol	1 2
Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1
	methanol	2 3. 3 9 4		methanol	2 3. 3 9 4		methanol	2 3. 3 9 4
	DMF	6 0		DMF	6 0		DMF	6 0
Fluorescent Dye	rhodamine B	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	T P B tetraphenyl -butadiene	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	quinacridone	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)

Table 6

(Example 6)

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)
Precursor	PPV -precursor	0. 3 7 5	Precursor	PPV -precursor	0. 3 7 5	Precursor	PPV -precursor	0. 3 7 5
Wetting Agent	glycerin	5	Wetting Agent	glycerin	5	Wetting Agent	glycerin	5
	diethylene -glycol	1 0		diethylene -glycol	1 0		diethylene -glycol	1 0
Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1
	methanol	2 3. 3 9 4		methanol	2 3. 3 9 4		methanol	2 3. 3 9 4
	DMF	6 0		DMF	6 0		DMF	6 0
Fluorescent Dye	rhodamine B	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	coumarin 138	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	Without Fluorescent Dye	—

Table 7

(Example 7)

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)
Precursor	CN-PPV -precursor	0. 3 7 5	Precursor	CN-PPV -precursor	0. 3 7 5	Precursor	CN-PPV -precursor	0. 3 7 5
Wetting Agent	glycerin	5	Wetting Agent	glycerin	5	Wetting Agent	glycerin	5
	diethylene -glycol	1 0		diethylene -glycol	1 0		diethylene -glycol	1 0
Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1
	methanol	2 3. 3 9 4		methanol	2 3. 3 9 4		methanol	2 3. 3 9 4
	DMF	6 0		DMF	6 0		DMF	6 0
Fluorescent Dye	Without Fluorescent Dye	—	Fluorescent Dye	distyryl -biphenyl	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	quinacridone	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)

(Comp. Ex. 1)

Table 8

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
	Composition	Amount of Content (wt%)	Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)
			Host	Alq ₃		Host	Alq ₃	
Host	Alq ₃	99.0	Host	Alq ₃	82.1	Host	Alq ₃	98.95
Dopant	DCM-1	1.0	Dopant	TPB	17.9	Dopant	coumarin 6	1.05
Wetting Agent	—	—	Wetting Agent	—	—	Wetting Agent	—	—
	—	—		—	—		—	—
Polar Solvent	—	—	Polar Solvent	—	—	Polar Solvent	—	—
	—	—		—	—		—	—
	—	—		—	—		—	—

Table 9

(Comp. Ex. 2)

Red Luminescent Layer		Blue Luminescent Layer		Green Luminescent Layer	
Composition	Amount of Content (wt%)	Composition	Amount of Content (wt%)	Composition	Amount of Content (wt%)
Host	Alq ₃	Host	Alq ₃	Host	Alq ₃
Dopant	DCM-1	Dopant	TPB	Dopant	coumarin 6
Wetting Agent	glycerin	Wetting Agent	glycerin	Wetting Agent	glycerin
	DEG		DEG		DEG
Polar Solvent	chloroform	Polar Solvent	chloroform	Polar Solvent	chloroform
	DMF		DMF		DMF
	24.0		7.1		23.95
	1.0		17.9		1.05
	5		5		5
	10		10		10
	10		10		10
	50		50		50

Table 10

[illegible]

Table 11

	Stability in Film Formation		
	R	G	B
Example 1	○	○	○
Example 2	○	○	○
Example 3	○	○	○
Example 4	○	○	○
Example 5	○	○	○
Example 6	○	○	○
Example 7	○	○	○
Comp. Ex. 1	○	△	×
Comp. Ex. 2	Impossible to form pattern		

FIG. 1

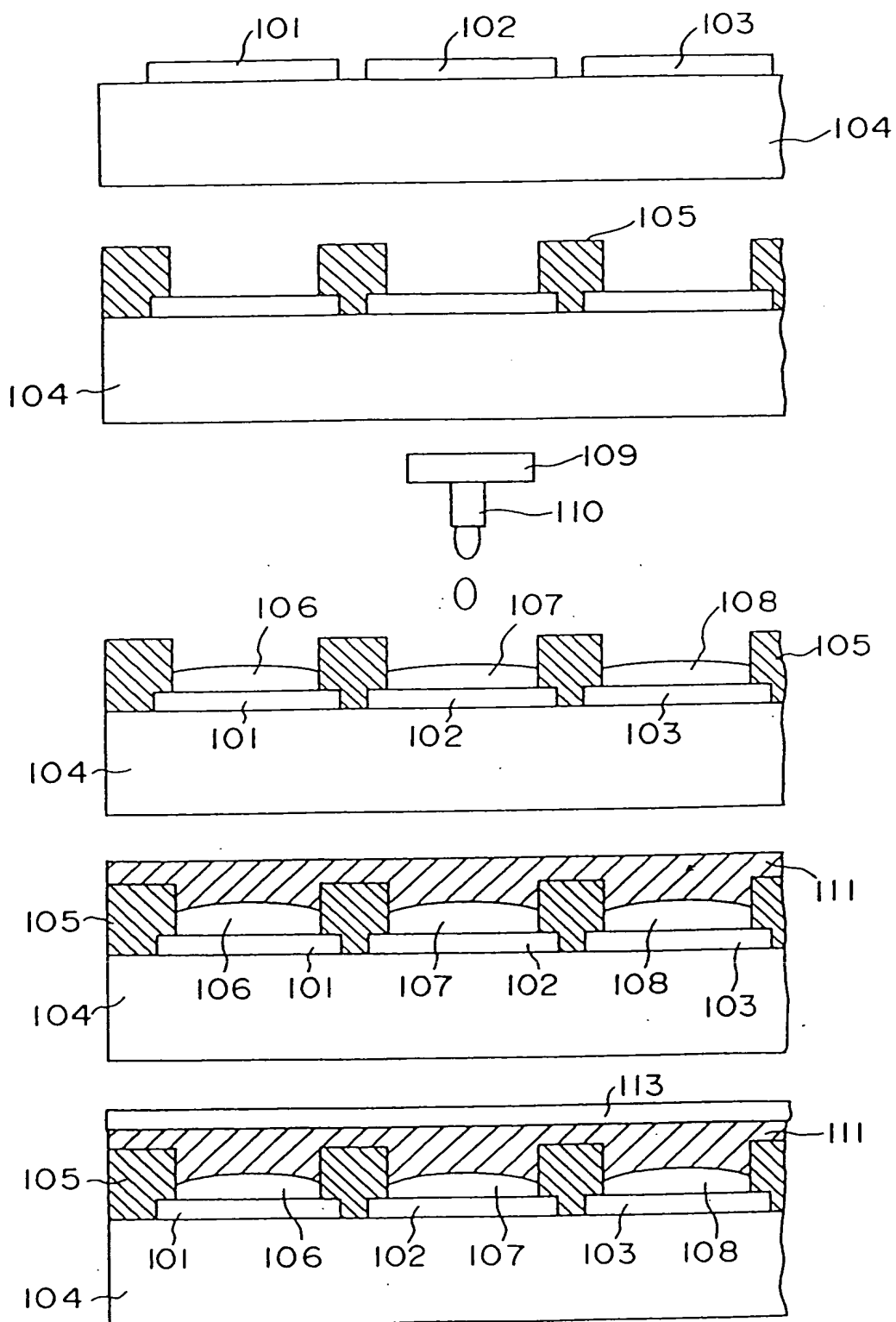


FIG. 2

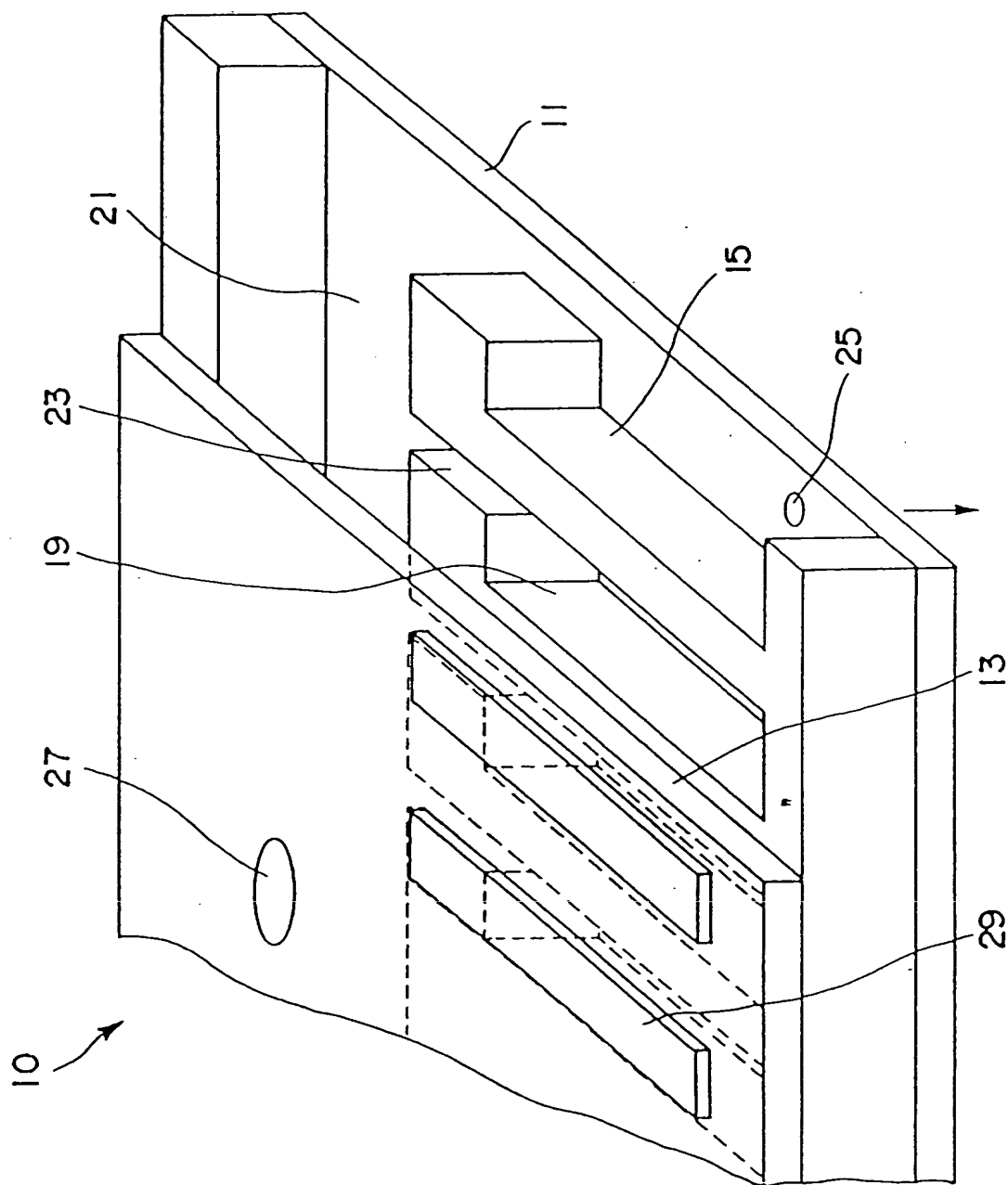
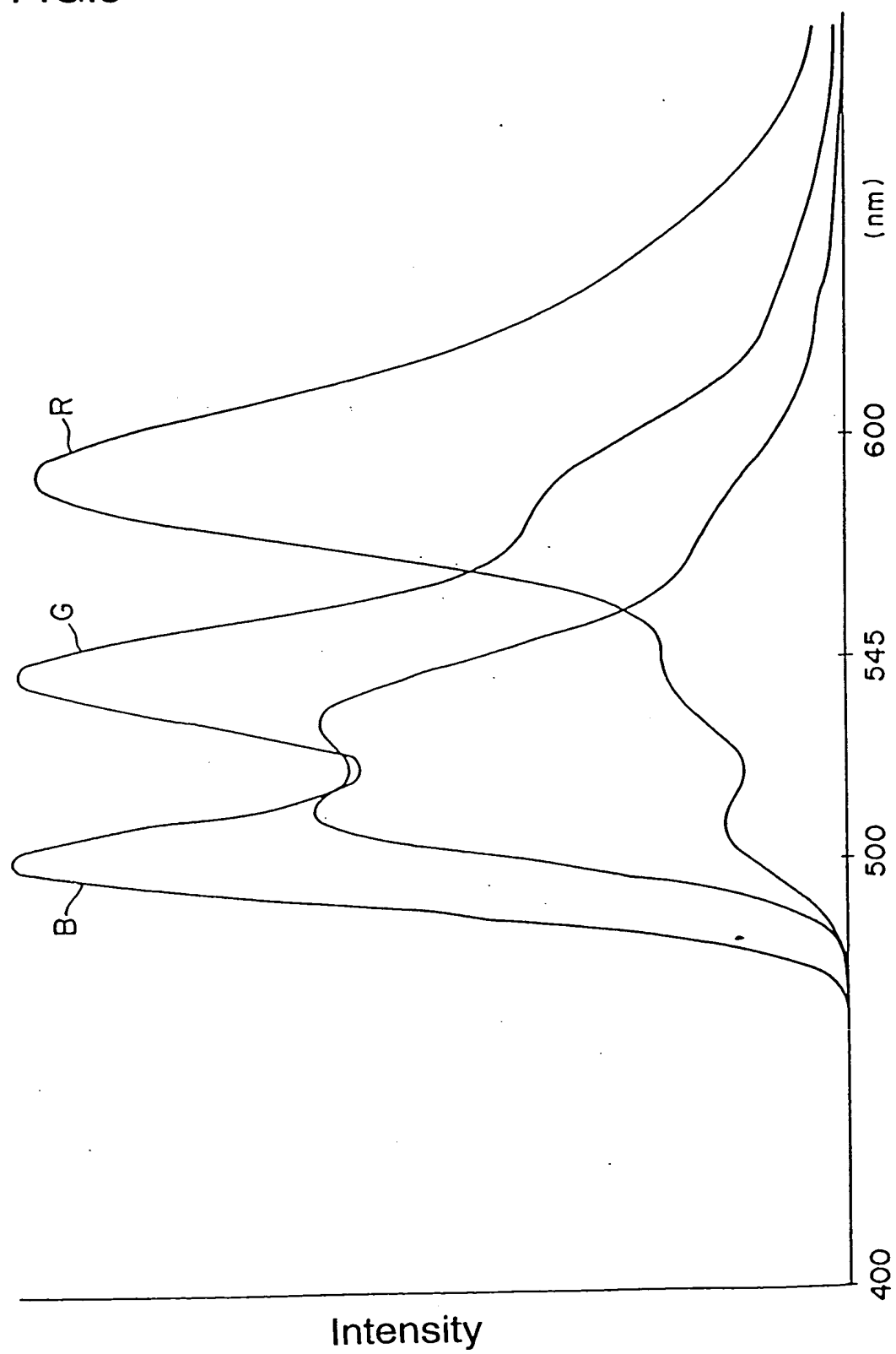
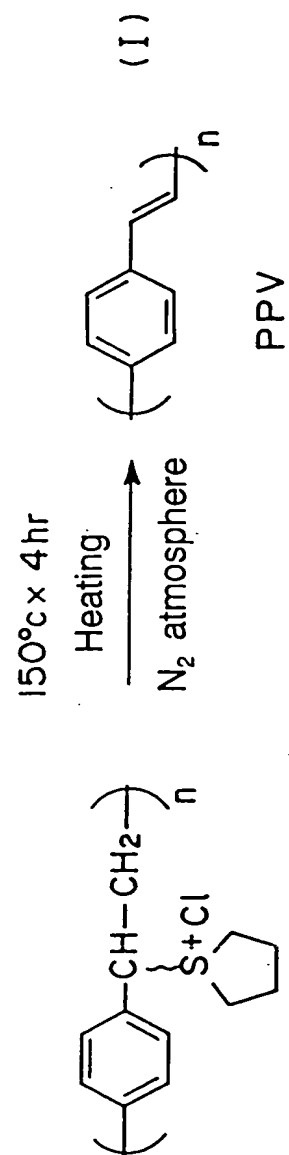


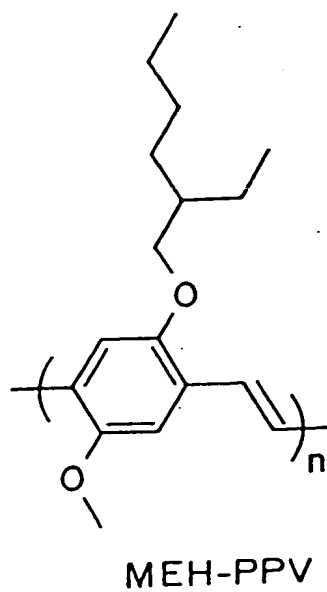
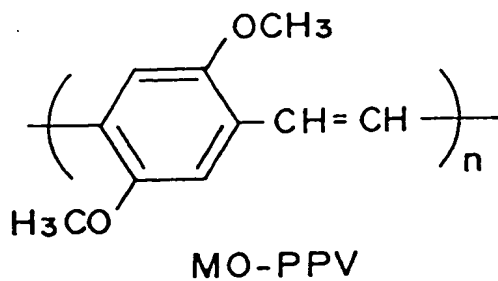
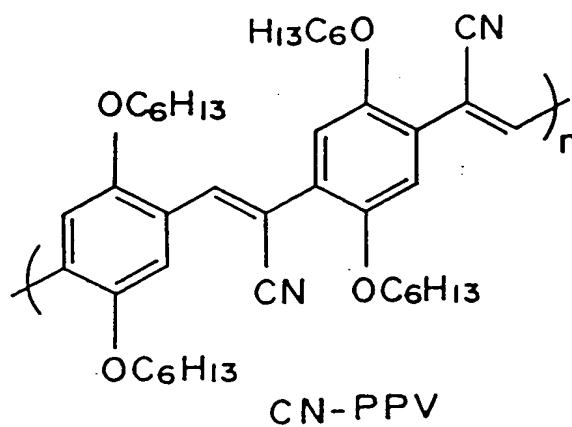
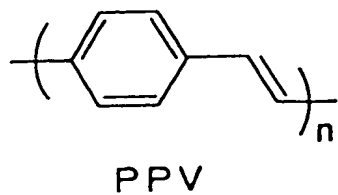
FIG.3



Chemical Formula 1



Chemical Formula 2



(II)